Benthic respiration on the northeastern shelf of the Gulf of Cádiz (SW Iberian Peninsula)

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ABSTRACT: Benthic fluxes of dissolved oxygen, total alkalinity, inorganic carbon and methane were determined *in situ* by benthic chamber deployments at 9 stations (depth range: 8 to 34 m) on the northeastern near-shore continental shelf of the Gulf of Cádiz (SW Iberian Peninsula) during 3 cruise periods (June 2006, November 2006 and February 2007). Sediment oxygen uptake and dissolved inorganic carbon fluxes, which ranged respectively from 9 to 27 mmol O_2 m^{-2} d^{-1} and from 18 to 58 mmol C m^{-2} d^{-1}, showed a good linear correlation with the organic carbon content of surface sediments (range: 0.25 to 1.18% dry wt). Benthic alkalinity fluxes were corrected for the influence of NH_4^+ and NO_3^- + NO_2^- fluxes, and the upper and lower limits for carbon oxidation rates (C_{ox}) were constrained by considering 2 possible scenarios: maximum and minimum contribution of $CaCO_3$ dissolution to corrected alkalinity fluxes. The averages of the calculated minimum and maximum C_{ox} values ranged from 14 to 46 mmol C m^{-2} d^{-1}. Benthic fluxes of methane were very variable, ranging from 0.9 to 24 µmol CH_4 m^{-2} d^{-1}, and represented only about 0.02% of the mineralized carbon. Two regions were differentiated by sediment properties and location: one off the Guadalquivir River mouth, which showed higher carbon remineralization, and another in the Bay of Cádiz and neighboring shelf. The mean carbon oxidation rate estimated for the entire study site was 28 ± 8 mmol C m^{-2} d^{-1}. The average ratio of carbon oxidation to oxygen uptake was 1.6 ± 0.3, indicating the importance of anaerobic mineralization processes and the storage of reduced metabolites.

KEY WORDS: Benthic fluxes · Carbon mineralization · Coastal · Dissolved inorganic carbon · Dissolved oxygen · Total alkalinity · Dissolved methane · Gulf of Cádiz

INTRODUCTION

Continental shelves represent the transition zone between the continents and the open ocean and are very important sites in the biogeochemical cycling of organic matter. In spite of their relatively small surface (<10% of global oceanic area), primary productivity in continental shelves accounts for ~25% of total oceanic production (Wollast 2002). In addition to this high primary productivity, continental shelves receive large amounts of terrestrial organic matter and nutrients, mainly through rivers. More than 95% of the organic carbon supplied to the shelves by primary production and continental input is mineralized in the water column and sediments (de Haas et al. 2002). Shelf sediments, because of the shallow water column (<200 m water depth), are rich in organic carbon and thus are sites of intense organic matter mineralization and nutrient recycling, playing a major role in the biogeochemistry and ecology of these systems (e.g. Berelson et al. 2003, Jahnke et al. 2005, Alongi et al. 2007).

The measurement of solute fluxes across the sediment-water interface can be used to quantify benthic organic matter mineralization rates and to explore the

role of the different oxidation pathways. The organic matter that reaches the sediment is degraded to inorganic constituents through a complex sequence of fermentative and respiratory microbial processes that use different terminal electron acceptors as oxidants. Whereas aerobic respiration is the most effective oxidation process and takes place in the uppermost oxic sediment layer, oxygen can be rapidly consumed in the first few millimeters of organic rich sediments (Revsbech et al. 1980) and, therefore, other terminal acceptors such as NO_3^-, oxides of Mn and Fe, and SO_4^{2-} are subsequently used as oxidants (Canfield 1993). Sulfate reduction is typically considered the dominant anaerobic pathway in coastal marine sediments and can account for 10 to 90% of the total C oxidation (Jørgensen 1982, Canfield 1993). Once sulfate is depleted, the organic matter is degraded through various fermentative processes and methanogenesis to CH_4 and CO_2. The biogenic benthic production of CH_4, which is a potent greenhouse gas and an important compound of atmospheric chemical cycles, often represents a small contribution to the C-cycle in coastal marine sediments (e.g. Hopkinson et al. 1999, Alongi et al. 2005) but may become significant for the global atmospheric emissions in coastal environments (Bange 2006, Barnes et al. 2006). However, the anaerobic oxidation of CH_4 by sulfate-reducing bacteria significantly limits the flux of CH_4 to the water column (Martens & Berner 1974, Valentine 2002).

The Gulf of Cádiz, given its geographical position connecting the Mediterranean Sea and the Atlantic Ocean through the Strait of Gibraltar, its extraordinary commercial interest for fisheries, and the influence that the Mediterranean outflow has on the large-scale North Atlantic circulation has, in the last few decades, attracted the attention of many physical and biological oceanographers (e.g. Vargas et al. 2003, Lobo et al. 2004, Huertas et al. 2006, Navarro & Ruiz 2006, Navarro et al. 2006, García-Lafuente & Ruiz 2007). Specifically, coastal waters in the northeastern shelf of the Gulf of Cádiz sustain the highest primary productivity of the basin and are tightly linked to meteorological and hydrodynamical conditions, presenting a strong seasonality (Vargas et al. 2003, Navarro & Ruiz 2006). However, no attempt has been made to date to investigate the role of benthic biogeochemistry and to quantify benthic mineralization processes in these shelf sediments. Documented benthic flux measurements in this region have only been performed in shallower salt-marsh sediments of the inner Bay of Cádiz (e.g. Forja et al. 2004, Ortega et al. 2008, Ferrón et al. 2009a). This work presents the results derived from *in situ* benthic chamber incubations performed in the northeastern shelf of the Gulf of Cádiz during 3 periods of the year, corresponding to summer, autumn and

winter. Benthic fluxes of dissolved oxygen (F_{DO}), total alkalinity (F_{TA}), inorganic carbon (F_{DIC}) and methane (F_{CH4}) are reported and the total organic carbon mineralization rates were estimated and discussed.

MATERIALS AND METHODS

Study site. The study was performed on the northeastern shelf of the Gulf of Cádiz, which is located on the southwestern coast of the Iberian Peninsula (Fig. 1). The Gulf of Cádiz is a wide basin with a key geographical location, as it is the place where the North Atlantic Ocean and the Mediterranean Sea meet through the Strait of Gibraltar. The basin is influenced by the dense plume of Mediterranean water that crosses the strait and by the freshwater inputs of several rivers that drain into the gulf, such as Guadiana, Guadalquivir, Tinto and Odiel. The Guadalquivir River is the main fluvial source draining into the Gulf of Cádiz margin, with a mean annual water discharge of 160 $m^3 s^{-1}$ (Van Geen et al. 1997). The circulation in the northeastern shelf of the Gulf of Cádiz is mainly controlled by the North Atlantic Surface Water (NASW), which flows towards the east and southeast to the Strait of Gibraltar, as well as by an intermittent counter current system, which seems to be strongly linked to the wind regime (Lobo et al. 2004). In particular, coastal waters near the mouth of the Guadalquivir River and the Bay of Cádiz present the highest primary production within the Gulf of Cádiz (Navarro & Ruiz 2006). Moreover, this region displays the greatest range of temperature variation throughout the year, being characterized by warmer and colder waters than
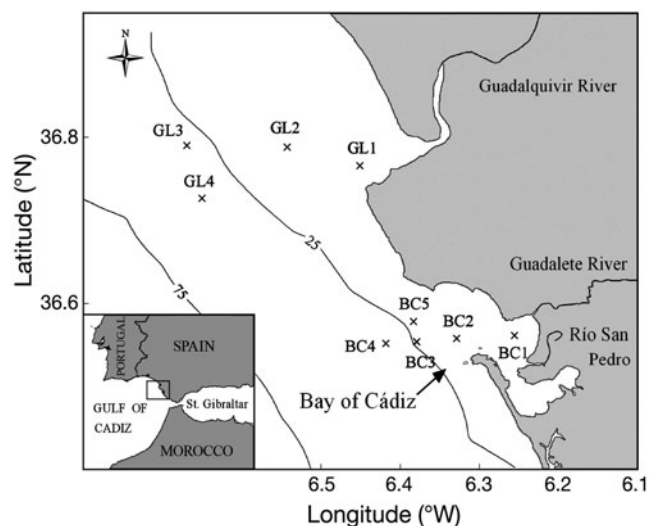

Fig. 1. Near-shore northeastern shelf of the Gulf of Cádiz showing the sampling stations and the location of the rivers and the Bay of Cádiz. Isolines represent the bathymetry in meters

the rest of the basin during summer and winter, respectively (Vargas et al. 2003, Navarro & Ruiz 2006). Phytoplankton distribution in this sector of the gulf is tightly coupled to meteorological and hydrodynamic conditions (Navarro & Ruiz 2006). For example, the predominance of western winds is always linked to the generation of upwelling events and therefore to an increase in primary production, whereas easterlies lead to a decrease in phytoplankton (Navarro & Ruiz 2006). Furthermore, the alternation of mixing and stratification periods in the region affects the position of the nutricline and thus also regulates the primary production (Navarro et al. 2006).

The data reported in this work were collected during three 12-d cruises on board the RV 'Mytilus' covering 3 seasonal periods: June 2006, November 2006 and February 2007. Nine sampling stations were selected for the study of benthic fluxes in 2 different field areas: one in the Bay of Cádiz and its neighboring outer region (BC1–BC5) and the other off the mouth of the Guadalquivir River (GL1–GL4) (Fig. 1). GL stations were located on the Guadalquivir submarine prodelta, which is characterized by a high fluvial supply and a moderate hydrodynamic regime (Lobo et al. 2004), whereas BC stations were located in a more energetic area affected by the tidal currents between the Bay of Cádiz and the outer shelf. Sediments in the study site are mainly siliciclastic with 25% of bioclastic carbonates, predominantly calcite (Gutiérrez-Mas et al. 2003).

At each station, vertical profiles of temperature, salinity and dissolved oxygen (DO) were obtained at the beginning of each chamber incubation, with a Seabird CTD probe coupled with a Seabird 43. Surface and bottom water samples were obtained for analyses of dissolved methane.

***In situ* benthic flux measurements.** *In situ* benthic flux chamber incubations were performed using a stirred benthic chamber (Ferrón et al. 2008). The incubations were performed during the day and lasted around 8 h. The cylindrical opaque PVC chamber (0.8 m inner diameter, 0.28 m height) covered 0.50 m^2 of sea-bottom and ~140 l of overlying water. The chamber was slowly lowered to the bottom from the ship with a crane. An 8 cm rim assured proper insertion of the chamber into the sediment. The contact of 3 mechanical devices, equipped with reed switches, served to verify proper landing of the chamber on the sea-bottom. The same procedure was applied to confirm the closure of 3 lids, which remained open during the landing process and were electronically closed when the chamber was placed on the bottom. Water inside the chamber was stirred by means of 3 external submersible centrifugal pumps, to avoid stratification and simulate natural conditions. Current velocity inside the chamber could be controlled by regulating the output voltage applied to

the pumps. Inside the chamber, sensors for temperature (SBE-39), pH (SBE-18), oxygen (SBE-43) and turbidity (Seapoint Turbidity Meter) provided continuous recording of these variables during the incubations. A 2-way radio communication system (SATELLINE-3AS, SATEL) was used for data acquisition and monitoring of the incubation in real time.

Discrete 50 ml samples were collected at pre-set time intervals by means of a multiple water sampler provided with 12 syringes. Water samples were filtered (0.45 μm) on board for the analysis of pH and alkalinity. Samples for methane analysis were, immediately after chamber recovering, carefully drawn into 25 ml air-tight glass bottles, preserved with saturated mercuric chloride and sealed with Apiezon® grease, and stored in the dark until analysis in the laboratory.

Sediment analysis and suspended particulate matter. The surface sediment at the different stations was sampled using a box-corer (15 cm × 10 cm), and the top cm was analyzed for total C and N composition and organic C content. Total C and N were measured in dried sediment using a CHNS-932-LECO elemental analyzer after Cr_2O_3 and $AgCo_3O_4$ catalyzed oxidation and segregation on a Haysep-Q-column. The organic C content in surface sediments was determined by chemical oxidation (Gaudette et al. 1974, El Rayis 1985) with a standard deviation of ±0.25%.

In addition, surface sediment samples were taken with a Van Veen drag to measure grain size distribution, which was determined by sieving and the fraction <63 μm by means of a laser diffraction analyzer. Analysis of grain size statistics was carried out using the software GRADISTAT (Blott & Pye 2001).

Water sample analytical methods. Alkalinity and pH were analyzed in duplicate 10 ml samples by potentiometric titration using a Metrohm 794 analyzer with glass combination electrodes (Metrohm, ref. 6.0210. 100). The titration was done with 0.1 M HCl in 0.7 M NaCl. The total alkalinity was computed from the second point of inflection by means of the Gran functions, taking into account the corrections for sulfate (Dickson 1990). For the dissociation of dissolved inorganic carbon (DIC), we used the acidity constants (K_1 and K_2) proposed by Lueker et al. (2000) in the total pH scale. The method was validated with reference standards provided by Dr. A. Dickson (Scripps Institution of Oceanography, San Diego, CA, USA). The accuracy of the initial measurement of the sample pH was ±0.003, and of the total alkinity (TA) ±3 μM. The repeatability of alkalinity determinations based on the standard deviation of 7 replicates was 0.2%.

Dissolved CH_4 concentrations were determined with a gas chromatograph (Varian CX 3600). In-syringe head space equilibration was used to extract the dissolved gases from the water samples. The temperature

of equilibration (±0.1°C) was registered by a thermometer (P500 Dostman electronic). Helium was used as the carrier gas (30 ml min⁻¹), and gases were separated in a 4.5 m × 1/8-inch stainless steel column packed with 80/100 Porapack N and a 1.5 m × 1/8-inch Molecular Sieve 5A column. CH_4 was measured with a flame ionization detector operated at 300°C. The detector was calibrated using 3 standard gas mixtures that were made and certified by Air Liquide (France), with certified CH_4 concentrations of 0.489, 1.07 and 2.53 ppmv. The precision of the method, including the equilibration step, expressed as the coefficient of variation based on replicate analysis (n = 25) of a seawater sample saturated with CH_4, was 4.8%. The concentrations of the gases in the water samples were calculated from the concentrations measured in the head space using the functions for the Bunsen solubilities given by Wiesenburg & Guinasso (1979).

Flux calculation. Fluxes across the sediment-water interface were calculated as the product of the chamber height and the slope of the linear regression of the concentration time series. Errors in benthic fluxes were determined as the error of the slope derived from the data fit, augmented by the height of the chamber using standard error propagation techniques, but considering the height as a constant (since the uncertainty in the height is not known).

RESULTS

Water column characteristics

Surface and bottom water characteristics determined at each station at the beginning of chamber deployments are plotted in Fig. 2. Water temperature presented a wide range of variation, from a maximum of 24°C in the summer period to a minimum of 12°C during the winter. During summer, higher surface temperatures were observed in the northern part as a consequence of the river discharge. Temperature differences between surface and bottom waters were only observed during the summer, mostly at GL sites, where they reached values of up to 6.5°C. During autumn and winter, a slight offshore-inshore temperature gradient was observed, decreasing towards the coast. Salinity ranged from 33.7 to 36.7 and was strongly influenced by the freshwater inputs coming from land, mostly off the Guadalquivir River. These results agree with previously reported data in this sector of the Gulf of Cádiz, which presents considerable seasonal variations that are mainly affected by the river discharge and the meteorological conditions (Huertas et al. 2006, Navarro & Ruiz 2006).

Bottom water oxygen concentrations were significantly lower during the summer than during autumn and winter (t-test, p < 0.02), with saturation values ranging from 79 to 95, 86 to 99 and 95 to 99%, respectively.

Bottom and surface waters were in all cases oversaturated with methane with respect to the atmosphere. The concentration of dissolved methane in the water column ranged from 4 to 57 nM. The highest concentrations were reported in BC1, located in the Bay of Cádiz (Fig. 1), where saturations varied between 580% and 2040%. At BC stations, the highest concentrations were observed during the winter in surface waters, whereas the lowest were reported in autumn. At GL stations, the concentration of methane presented less spatial variability but fluctuated seasonally, showing highest concentrations during the summer and lowest during the winter.

Sediment characteristics

Average sediment characteristics at each site are presented in Table 1. Granulometric analysis showed that GL stations were characterized by poorly sorted mud or sandy mud sediments. BC sediments were also poorly or very poorly sorted, with the coarse material being mainly calcareous shell fragments. Grain size in these stations varied between muddy sand in BC1, slightly gravely muddy sand in BC2 and BC3, gravely muddy sand in BC4 and slightly gravely sandy mud in BC5.

The OC content in surface sediments ranged from 0.25 to 1.18% and was significantly higher at GL stations than at BC stations (t-test, p < 0.01). A good negative logarithmic correlation was observed between the OC content and the median grain size of sediments ($r^2 = 0.84$). Sediment total nitrogen content (TN), ranging between 0.04 and 0.18%, was also significantly lower at BC stations than at GL stations (t-test, p < 0.01). Surface OC and TN content showed a good linear correlation ($r^2 = 0.96$). Surface sediment C:N molar ratios were not significantly different in GL and BC sites, and showed average values that ranged from 7.0 to 9.5.

Benthic fluxes

Two representative examples of the time course of dissolved oxygen, total alkalinity, inorganic carbon and methane concentrations during a benthic chamber incubation are plotted in Fig. 3. The trends in the rest of the incubations are similar to these examples. Benthic fluxes measured at the 9 sites in the northeastern shelf of the Gulf of Cádiz during June 2006, November 2006 and February 2007 are plotted in Fig. 4. F_{TA}, F_{DIC} and F_{CH4} were on all occasions directed out of the sediment,

whereas F_{DO} were directed into the sediment. F_{DO}, F_{TA} and F_{DIC} in BC sites were smaller than those reported by Forja et al. (2004), which were measured during the years 1988 and 1989 in a shallower nearby station of the inner Bay of Cádiz characterized by higher sediment organic matter content (2.65 % dry wt).

Oxygen uptake rates ranged from 9 to 27 mmol m^{-2} d^{-1} and were significantly higher at GL sites (21 ± 5 mmol m^{-2} d^{-1}; *t*-test, p < 0.01) than at BC sites (15 ± 5 mmol m^{-2} d^{-1}). The same pat-

Table 1. Depth (m), averaged from the 3 seasons sampled of surface sediment content of organic carbon (OC) (% dry wt), inorganic carbon (IC) (% dry wt), total nitrogen (TN) (% dry wt), molar C:N ratio and median grain size (D_{50}) (µm) for each station. Values are means ±1 SD

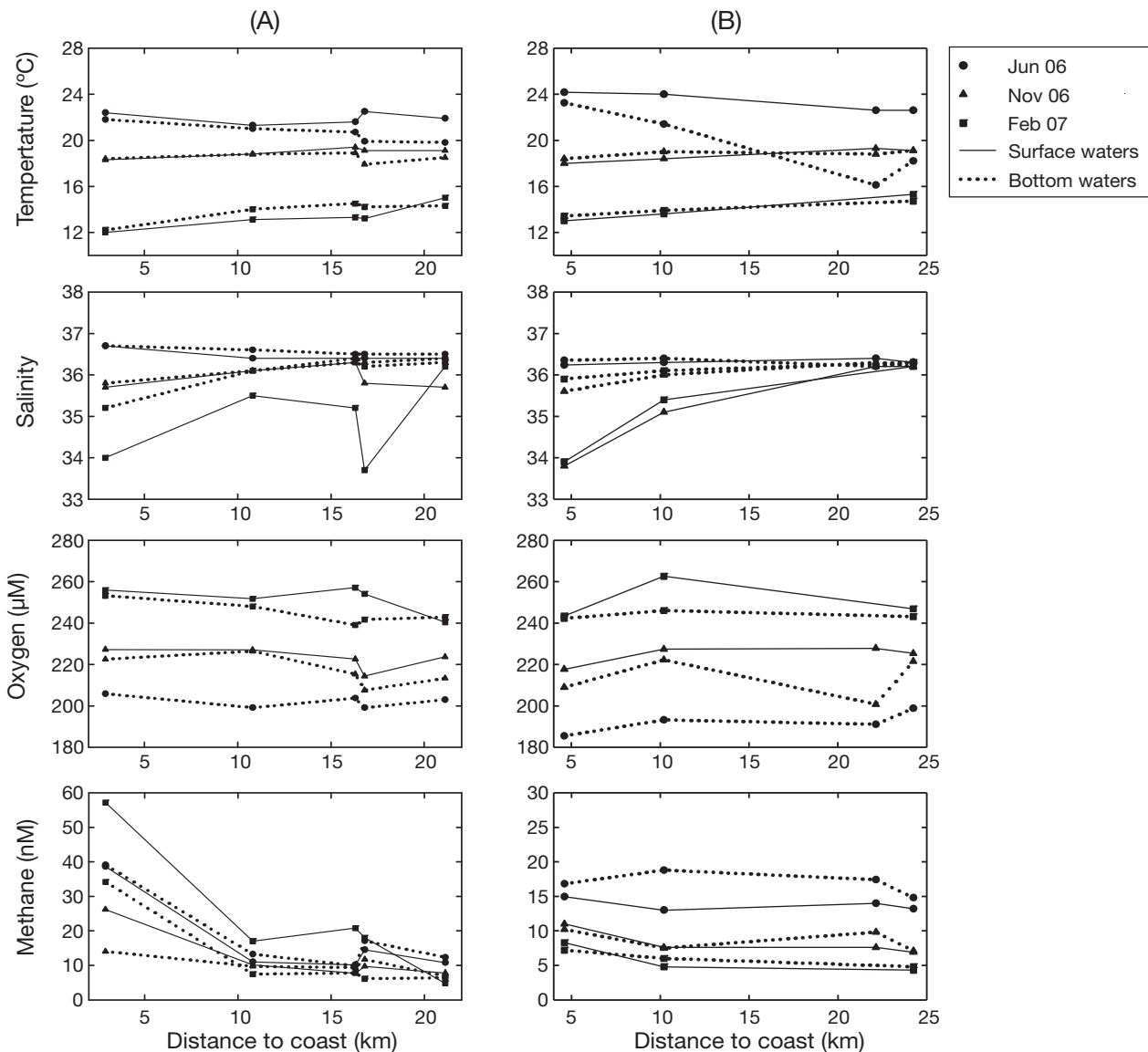| Station	Depth	OC	IC	TN	C:N	D_{50}
BC1	8	0.25 ± 0.01	2.70 ±0.21	0.04 ± 0.01	8.19	372
BC2	18	0.47 ± 0.15	3.04 ± 0.20	0.06 ± 0.02	8.80	61
BC3	22	0.29 ± 0.04	1.81 ± 0.14	0.03 ± 0.01	8.38	421
BC4	32	0.64 ± 0.03	3.05 ± 0.38	0.08 ± 0.01	8.83	78
BC5	22	0.75 ± 0.28	2.96 ± 0.24	0.12 ± 0.07	7.03	76
GL1	13	1.18 ± 0.25	3.50 ± 0.28	0.18 ± 0.03	7.85	12
GL2	18	0.83 ± 0.05	3.97 ± 0.07	0.11 ± 0.01	8.45	13
GL3	29	0.80 ± 0.07	3.55 ± 0.44	0.12 ± 0.01	9.45	27
GL4	34	0.93 ± 0.03	3.91 ± 0.02	0.14 ± 0.01	7.69	6.8

Fig. 2. Surface and bottom water characteristics at the beginning of each chamber incubation vs. distance to the coast for (A) BC stations and (B) GL stations
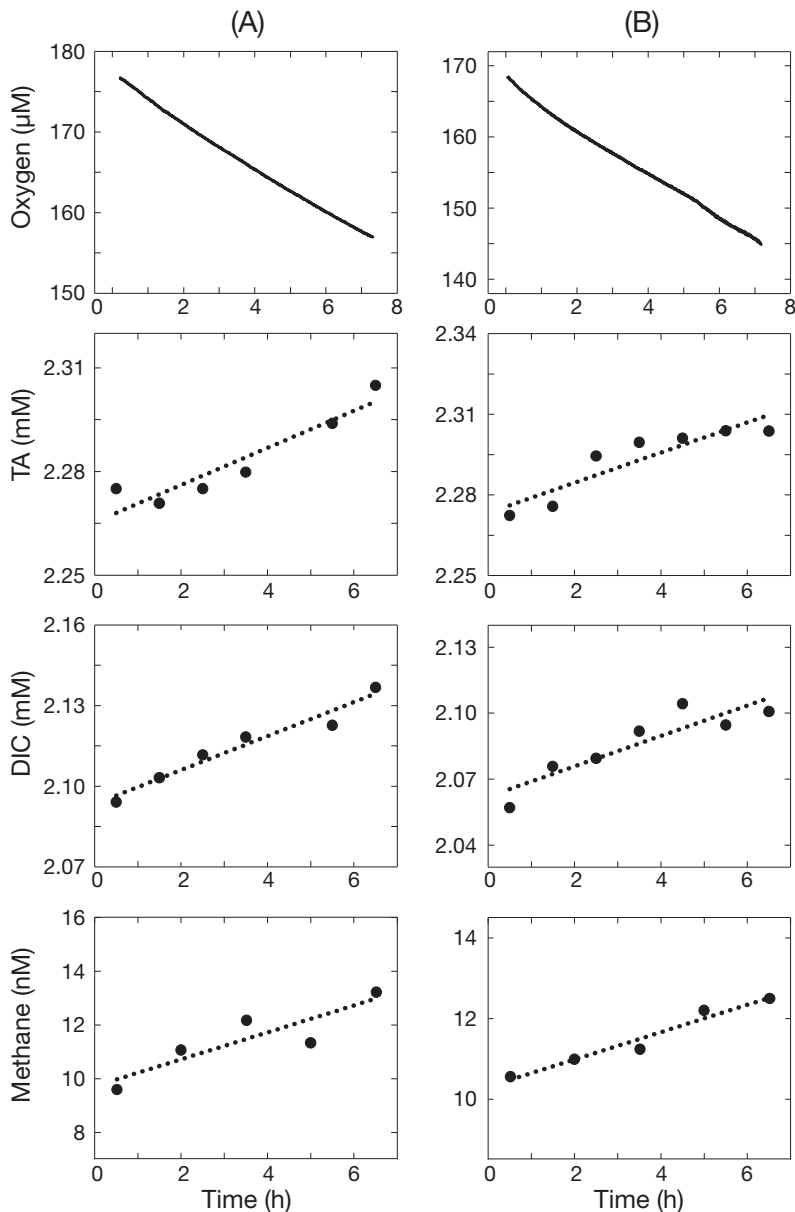
Fig. 3. Representative examples of the time course of dissolved oxygen, total alkalinity (TA), dissolved inorganic carbon (DIC) and dissolved methane concentrations in 2 chamber deployments made at (A) Stn BC2 and (B) Stn GL2

production could be significant even if only small amounts of light reach the sediment surface (Jahnke et al. 2000) and, consequently, our measurements would not integrate net benthic metabolism but only respiration.

Seasonal variability

Although benthic fluxes of dissolved inorganic carbon and oxygen were significantly higher in the summer than in the winter (*t*-test, p < 0.03), fluxes measured in autumn were not statistically different from those measured in summer or winter. The spatial variability observed among the stations was higher than the seasonal variations. Regional averages of benthic oxygen uptake and C mineralization are plotted in Fig. 5 for each period sampled. BC and GL regions show a similar pattern, presenting higher respiration rates in June compared to November and February. Seasonal variability on carbon mineralization rates has been reported in many other systems (e.g. Hopkinson et al. 1999, Berelson et al. 2003, Forja et al. 2004, Ståhl et al. 2004a) and may either reflect the diminution of reaction rates, diffusion rates and faunal activity with decreasing temperature, and/or the differences in the inputs of fresh organic matter, which may be associated to phytoplankton blooms or to changes in terrestrial inputs. This highlights the importance of having a seasonal coverage when studying benthic mineralization. On the other hand, no statistical seasonal differences were observed for alkalinity and methane fluxes.

DISCUSSION

Carbon mineralization rates

Benthic fluxes measured *in situ* with chambers integrate the net sum of the diagenetic reactions taking place in the sediment. Sediment oxygen uptake rate and the production of dissolved inorganic carbon (DIC) are generally considered as good representative measurements of the total organic carbon oxidation rate (C_{ox}) (Anderson et al. 1986, Canfield et al. 1993, Ståhl
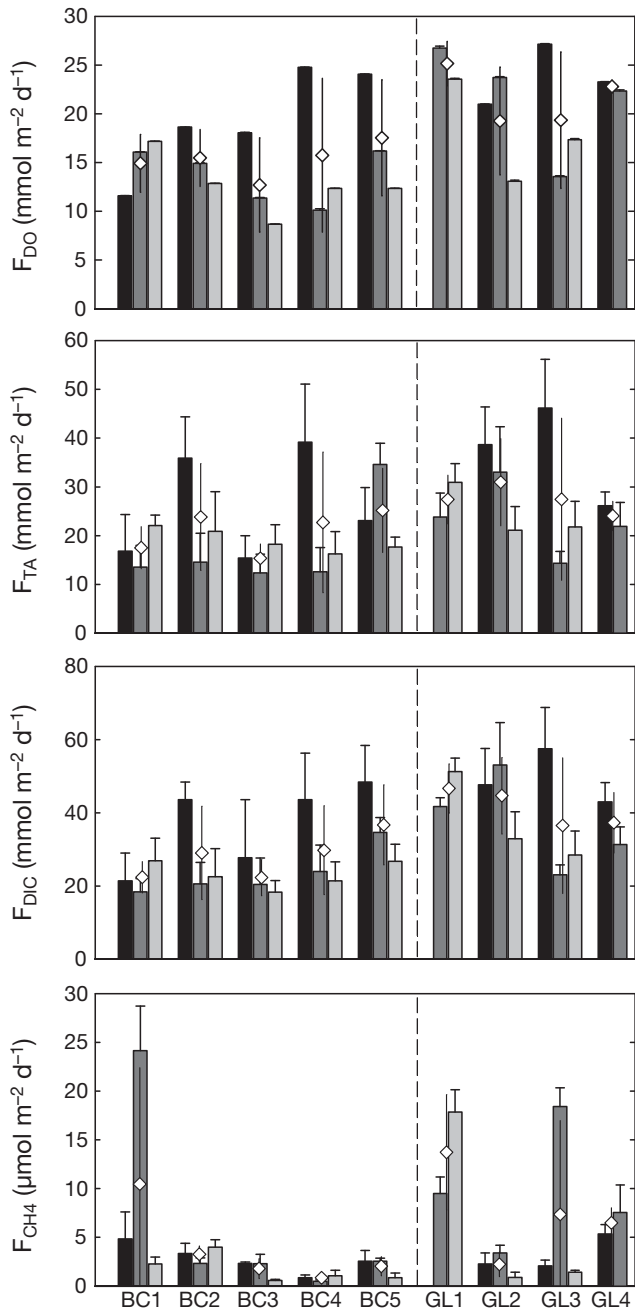
tern was also observed for F_{DIC}, with average fluxes for GL and BC stations of 41 ± 12 mmol m^{-2} d^{-1} and 28 ± 10 mmol m^{-2} d^{-1}, respectively. F_{DIC} and F_{TA} were of similar magnitude and presented a good linear correlation ($r^2 = 0.73$).

F_{CH4} were very variable and always positive, ranging from 0.9 to 24 µmol m^{-2} d^{-1}, although in most cases they were below 5.5 µmol m^{-2} d^{-1}. On a few occasions during the autumn and winter surveys, exceptionally higher methane fluxes were reported.

It should be taken into account that, due to the shallowness of the studied sites, benthic primary

Fig. 4. Benthic fluxes (F_{DO}: oxygen; F_{TA}: total alkinity; F_{DIC}: inorganic carbon; F_{CH4}: methane) measured at the different sampling stations during June 2006 (black bars), November 2006 (dark gray bars) and February 2007 (light gray bars). Error bars: uncertainties from the error in the slope of the data fit. Dashed line separates BC and GL regions. White diamonds: mean values for each site (±SD)

Fig. 5. Average oxygen uptake (F_{DO}) and flux of inorganic carbon (F_{DIC}) in each period for both sampling areas. Error bars are 1 SD

et al. 2004a,b, Glud 2008). In the study site, DIC fluxes were linearly correlated with oxygen uptake rates ($r^2 = 0.74$). Oxygen in sediments is used for aerobic respiration and for the re-oxidation of reduced inorganic products rel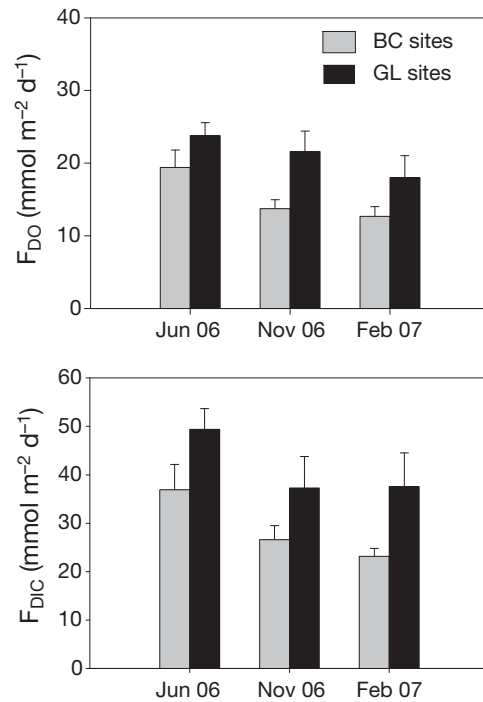eased during anaerobic mineralization (e.g. Mn^{2+}, Fe^{2+}, H_2S) (Canfield et al. 1993). The reduction of sulfate, iron oxides and manganese oxides, and the subsequent re-oxidation of Fe^{2+}, Mn^{2+} and H_2S by oxygen, have the same net stoichiometry as heterotrophic O_2 respiration (Jørgensen 1977, Canfield 1993), which means that oxygen is consumed at the same rate as carbon is oxidized. One exception is denitrification, the dissimilatory nitrate reduction to inert N_2 gas, which does not affect oxygen consumption. The use of oxygen uptake to estimate organic carbon mineralization is based on the assumption that oxygen is consumed in direct proportion to the total carbon oxidized by both aerobic and anaerobic pathways (Canfield et al. 1993). Therefore, oxygen uptake rates may fail to represent total C_{ox} when (1) denitrification is significant, (2) a considerable fraction of the reduced substances escapes oxidation either by being liberated to the water column or by getting buried in the sediment (e.g. FeS) or (3) the production and oxidation of reduced solutes are not at steady state. On the other hand, the flux of DIC is often considered as a better proxy of C_{ox} as it ultimately occurs in both aerobic and anaerobic carbon mineralization processes, with the exception of methane formation, although it is also influenced by the dissolution of $CaCO_3$ (Anderson et al. 1986). The contribution of $CaCO_3$ dissolution to DIC fluxes could be constrained by measuring Ca^{2+} benthic fluxes, although unfortunately these data were not

available in this study. In any case, benthic fluxes of total alkalinity can provide an insight into the relative importance of $CaCO_3$ dissolution rates. The flux of alkalinity is affected by the dissolution of $CaCO_3$ and some organic carbon mineralization processes, such as the release of ammonium, denitrification, nitrification, sulfate reduction, and manganese and iron reduction/oxidation processes (Berelson et al. 1996, 1998, Mucci et al. 2000). Table 2 summarizes the parameters calculated to understand carbon diagenesis in the study site. Following the method proposed by Berelson et al. (1996, 1998) and Hammond et al. (1999) to break down alkalinity fluxes, these were corrected for the contribution of ammonium and net denitrification by adding the fluxes of nitrate and nitrite and subtracting the flux of ammonium (taken from Ferrón et al. 2009b). This correction represented on average <5% of alkalinity fluxes. With this adjustment, corrected alkalinity fluxes (TA_{corr}) are only attributable to net sulfate reduction, to metal reduction/oxidation processes and to the dissolution of $CaCO_3$. Considering that only $CaCO_3$ dissolution contributed to corrected alkalinity fluxes, the upper limit for $CaCO_3$ dissolution rates can be calculated as $\frac{1}{2}TA_{corr}$ flux (Table 2), given that 2 equivalents of total alkalinity are produced per mole of $CaCO_3$ dissolved (Mucci et al. 2000). Maximum $CaCO_3$ dissolution rates ranged from 6 to 22 mmol m^{-2} d^{-1} (average

±SD, 11.3 ± 4.4 mmol m^{-2} d^{-1}), accountable on average for 35% of DIC fluxes. This is in line with the upper limit for the contribution of $CaCO_3$ dissolution to DIC fluxes (33%) calculated in sediments of a nearby salt marsh creek of the Bay of Cádiz (Ferrón et al. 2009a). In any case, the influence of $CaCO_3$ dissolution on DIC fluxes varies substantially in different coastal environments. Forja et al. (2004) calculated maximum dissolution rates to be 25 to 52% of DIC fluxes in different coastal ecosystems of the Iberian Peninsula. In central California Borderland sediments, Berelson et al. (1996) found that the dissolution of $CaCO_3$ represented between 3 and 27% of DIC fluxes. Hammond et al. (1999) found this contribution to be only about 5% of DIC fluxes in sediments of the Northern Adriatic Sea, whereas Anderson et al. (1986) found it to be <2% in Gullmar Fjord sediments (Skagerrak/North Sea Coast).

With the available information, it was possible to constrain the upper and lower limits of organic carbon oxidation rates in the study site. The lower limit of C_{ox} was calculated by subtracting maximum $CaCO_3$ dissolution rates from measured DIC fluxes, whereas the upper limit is given by measured DIC fluxes (Table 2), which would mean that $CaCO_3$ dissolution is negligible. If all the TA_{corr} flux is attributed to sulfate reduction, the upper limit for the amount of carbon oxidized by sulfate can be estimated, assuming the net stoi-

Table 2. Date of sampling (d/mo/yr), corrected alkalinity fluxes (TA_{corr}) and estimated maximum $CaCO_3$ dissolution rates (Max DIS); minimum, maximum and average carbon oxidation rates (C_{ox}), maximum carbon oxidized by net sulfate reduction and Community Respiration Quotient (CRQ = C_{ox}/F_{DO}) for each station. Rate units are in mmol C m^{-2} d^{-1}

Site	Date	TA_{corr}	Max DIS	Min C_{ox}	Max C_{ox}	Average C_{ox}	Max C_{ox} by SO_4	CRQ
BC1	17.06.06	16.50	8.25	13.15	21.40	17.27	13.53	1.49
BC2	18.06.06	32.90	16.45	27.11	43.56	35.34	26.98	1.90
BC3	19.06.06	15.39	7.70	20.00	27.70	23.85	12.62	1.32
BC4	20.06.06	37.72	18.86	24.69	43.55	34.12	30.93	1.38
BC5	21.06.06	21.42	10.71	37.66	48.37	43.02	17.57	1.79
GL2	24.06.06	36.53	18.26	29.37	47.64	38.50	29.95	1.84
GL3	26.06.06	44.98	22.49	35.01	57.50	46.25	36.88	1.71
GL4	27.06.06	24.17	12.08	30.90	42.98	36.94	19.82	1.59
BC1	19.11.06	13.75	6.87	11.52	18.39	14.96	11.27	0.93
BC2	20.11.06	15.08	7.54	13.03	20.57	16.80	12.37	1.13
BC3	21.11.06	12.10	6.05	14.33	20.38	17.35	9.92	1.53
BC4	22.11.06	11.68	5.84	18.06	23.89	20.97	9.57	2.07
BC5	23.11.06	32.96	16.48	18.11	34.59	26.35	27.03	1.63
GL1	29.11.06	22.19	11.09	30.62	41.71	36.16	18.19	1.35
GL2	28.11.06	31.17	15.59	37.46	53.05	45.26	25.56	1.91
GL3	27.11.06	13.32	6.66	16.40	23.06	19.73	10.92	1.45
GL4	26.11.06	21.52	10.76	20.54	31.30	25.92	17.65	1.16
BC1	31.01.07	21.45	10.72	16.15	26.88	21.51	17.59	1.25
BC2	01.02.07	21.68	10.84	11.66	22.50	17.08	17.78	1.33
BC3	02.02.07	17.47	8.74	9.57	18.31	13.94	14.33	1.61
BC4	03.02.07	15.15	7.57	13.80	21.37	17.59	12.42	1.42
BC5	04.02.07	18.83	9.42	17.31	26.72	22.02	15.44	1.78
GL1	06.02.07	26.49	13.25	37.98	51.22	44.60	21.72	1.89
GL2	07.02.07	21.11	10.56	22.32	32.87	27.59	17.31	2.11
GL3	08.02.07	20.43	10.21	18.26	28.47	23.37	16.75	1.35

chiometry for the reaction of sulfate reduction in the presence of iron-oxyhydroxides (Fe(OH)$_3$), with an average organic matter oxidation state of 0 and given the measured C:N ratio (Hammond et al. 1999). The maximum net sulfate reduction rates estimated this way ranged from 10 to 37 mmol C m^{-2} d^{-1}, accountable on average for 58% of DIC fluxes, which is very much in line with what Ferrón et al. (2009a) estimated for nearby salt marsh sediments of the Bay of Cádiz.

The upper and lower limits for C$_{ox}$ were in all cases within ±30% of their average. Thus, the averages of the maximum and minimum C$_{ox}$ values were considered as the most likely estimate of carbon mineralization, ranging from 14 to 46 mmol C m^{-2} d^{-1}. These values are within the range of carbon mineralization rates reported in the literature for other coastal environments (Canfield et al. 1993, Thamdrup & Canfield 1996, Berelson et al. 1998, 2002, 2003, Hopkinson et al. 2001, Ståhl et al. 2004a). Similarly to DIC fluxes and oxygen uptake rates, C$_{ox}$ rates were significantly higher in the summer than in the winter (*t*-test, p < 0.05), whereas C$_{ox}$ rates in autumn were not statistically different from summer and winter.

Although C$_{ox}$ rates were generally higher than benthic oxygen uptake rates, these 2 parameters were linearly correlated (r^2 = 0.74), which seems to indicate a coupling between anaerobic mineralization and the re-oxidation of reduced inorganic compounds. The C$_{ox}$:F$_{DO}$ ratios can be used to evaluate to what extent the production and oxidation of reduced anaerobic compounds are at a steady state and balanced at the time of investigation (Anderson et al. 1986, Glud 2008). However, the C$_{ox}$:F$_{DO}$ ratio is also determined by the composition of the organic matter that is being remineralized and by the end products of the mineralization process (Anderson et al. 1986). Assuming that a C$_{ox}$:F$_{DO}$ ratio equal to 1 indicates a steady state situation where anaerobic mineralization and the re-oxidation of reduced metabolites occur simultaneously, the C$_{ox}$:F$_{DO}$ ratios measured in the Gulf of Cádiz, which ranged on average from 0.9 to 2.1 (means ± SD: 1.6 ± 0.3), indicate that anaerobic mineralization is important and that there is a significant storage of reduced compounds over an annual period. The C$_{ox}$:F$_{DO}$ ratios measured in the Gulf of Cádiz are within the range reported in other coastal environments (Anderson et al. 1986, Forja et al. 2004, Ståhl et al. 2004a). Although the C$_{ox}$:F$_{DO}$ ratios can vary widely on a seasonal basis (Glud 2008), we found no significant differences between the seasons sampled.

Controls on organic matter mineralization

Organic matter mineralization was more intense in GL sites compared to BC sites (*t*-test, p < 0.01), and showed an average C$_{ox}$ of 23 ± 5 mmol C m^{-2} d^{-1} in the

GL region and 35 ± 5 mmol C m^{-2} in the BC region. Fig. 6a shows annually averaged carbon oxidation rates estimated for each sampling. Average F$_{DIC}$, F$_{DO}$ and C$_{ox}$ for each site were found to be strongly correlated with the organic carbon content of surface sediments (r^2 = 0.88, r^2 = 0.89 and r^2 = 0.90, respectively) (Fig. 6b). This pattern has been previously observed by other authors (e.g. Forja et al. 2004, Lansard et al. 2008) and suggests a dependence of carbon remineralization rates on the quantity of organic matter in surface sediments. Sedimentary organic matter consists of a mixture of more or less degradable fractions, and it is well established that one important factor controlling carbon oxidation rates is the quality (rather than the quantity) of the organic matter being mineralized (Arnosti & Holmer 2003, Ståhl et al. 2004a). However, in this study we did not observe any correlation between average F$_{DIC}$, F$_{DO}$ and C$_{ox}$ rates and average sediment C:N molar ratios. In contrast, Ståhl et al. (2004a,b) found significant relationships between organic carbon recycling rates and labile material (e.g. phytodetritus), whereas they observed no relationship between C$_{ox}$ and bulk sediment organic matter content. This discrepancy may indicate that the fraction of bulk organic carbon that is labile must be similar in all stations sampled, and also that the sediment C:N molar ratio may not be a good indicator in the study site of the quality of organic matter.
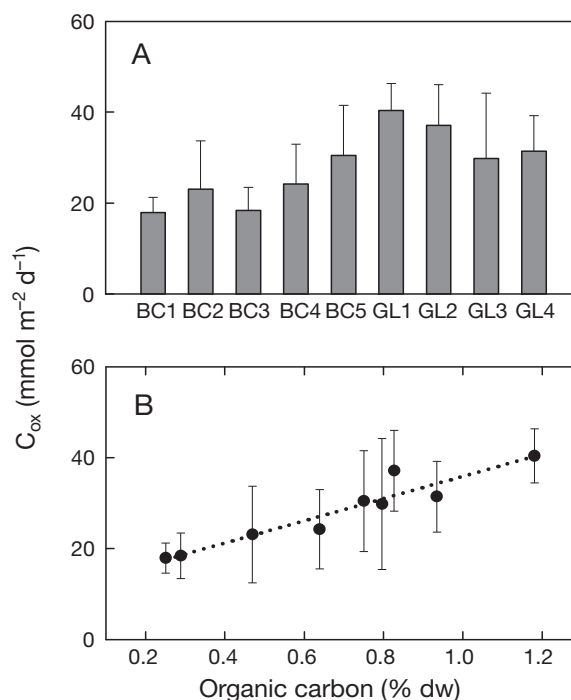

Fig. 6. (A) Annually averaged carbon oxidation rates (C$_{ox}$) (±SD) at each sampling site and (B) relationship between annually averaged C$_{ox}$ (±SD) at each sampling site and surface sediment organic carbon content (r^2 = 0.90)

As noted before, the seasonal variability in fluxes seemed to be less important than the region's own spatial variability, the latter presumably due to different sediment characteristics (e.g. organic carbon, C:N ratios, granulometries).

Dissolved methane benthic fluxes

In addition to the oxidative pathways of C mineralization, methanogenesis takes place in marine sediments preferentially via CO_2 reduction, since acetate is generally depleted by sulfate reducers (Reeburgh 2007) and thus represents a sink of dissolved inorganic carbon. Methanogenesis normally occurs after the sulfate pool has been exhausted, as sulfate-reducing bacteria compete with methanogens for the same substrates (Martens & Berner 1974). The fluxes of CH_4 across the sediment-water interface are then controlled by the transport of produced CH_4 to the sediment surface, which can be through molecular diffusion and/or bubble ebullition. Nearly all the CH_4 produced is oxidized anaerobically coupled to sulfate reduction (Valentine 2002), following the given reaction:

$$CH_4 + SO_4^{2-} \rightarrow HCO^{3-} + HS^- + H_2O$$

There are few documented measurements of net benthic CH_4 fluxes and, although some authors have pointed out the importance of marine sediments in atmospheric CH_4 emissions from coastal systems (Upstill-Goddard et al. 2000, Sansonse et al. 2004, Bange 2006), their quantitative contribution still remains unknown.

On the northeastern shelf of the Gulf of Cádiz, benthic dissolved CH_4 fluxes were always observable but relatively low, generally <10 μmol m^{-2} d^{-1}, except for a few occasions on which fluxes reached higher values of up to 24 μmol m^{-2} d^{-1}. Average CH_4 flux (5 ± 4 μmol CH_4 m^{-2} d^{-1}) represented on average only 0.02 % of the dissolved inorganic carbon flux derived from organic matter oxidation, which is in good agreement with previous results obtained in a shallow tidal creek located in the salt marsh area of the Bay of Cádiz (Ferrón et al. 2009a). The amount of methane that escapes to the water column can hence be neglected when using DIC fluxes as a proxy of carbon mineralization rates. However, although benthic CH_4 fluxes are negligible in terms of C mineralization, they potentially represent a considerable source of biogenic CH_4 to bottom waters in the study site (Ferrón et al. in press).

CONCLUSIONS

The annually averaged carbon oxidation rate for the entire study site was 28 ± 8 mmol C m^{-2} d^{-1}. BC sites showed lower respiration rates compared to GL sites, with average C_{ox} of 23 ± 5 mmol C m^{-2} d^{-1} for the former and 35 ± 5 mmol C m^{-2} for the latter site. The upper limit for $CaCO_3$ dissolution rates represents on average 35 % of measured DIC fluxes. The average C_{ox}:F_{DO} ratio for the entire study site was 1.6 ± 0.3, which indicates the importance of anaerobic mineralization processes and the storage of reduced metabolites. Carbon oxidation rates in the study site were mostly influenced by the organic carbon content of surface sediments, as reflected by the good linear relationship observed between both parameters ($r^2 = 0.90$).

Sediments were in all cases a source of CH_4 to the water column and, although benthic fluxes of this biogas represented in all cases a negligible fraction of DIC fluxes, they could potentially be a considerable source of biogenic CH_4 to bottom waters.

It is important to note that, whereas benthic oxygen uptake is often considered as a good representative measurement of organic carbon mineralization since it accounts for both aerobic respiration and the oxidation of reduced products derived from anaerobic mineralization, it may underestimate carbon mineralization rates as it does not account for denitrification and for the storage of reduced compounds or their possible release to the water column prior to oxidation. Therefore, a combination of both dissolved oxygen and dissolved inorganic carbon flux measurements is desirable when studying benthic respiration processes.

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